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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant: SHUICHI KANNO ET AL.

Serial No.: 09/005,006

Group Art Unit: 1754

Filed: JANUARY 9, 1998

Examiner: N. NGUYEN

Title: PROCESS FOR TREATING FLUORINE COMPOUND-
CONTAINING GAS

DECLARATION UNDER 37 C.F.R. § 1.132

Commissioner for Patents
Washington, D.C. 20231

Sir:

I, SHUICHI KANNO, am the first-named inventor of the present U.S. patent application and declare that:

1. I am a citizen of Japan, residing at 17-13, Ishinazaka-cho 1-chome, Hitachi city, Ibaraki, Japan.
2. I graduated from the material chemistry graduate course of the Engineering Department of Tohoku University in March 1992.
3. I began employment with Hitachi, Ltd. in April 1992.
4. I have read and understood U.S. Patent No. 6,069,291 (hereinafter, Rossin).

I. EXPERIMENTS

5. The following experiments were conducted under my supervision and control:

(a) Catalysts were made having a composition comprising 26.8% by weight of nickel oxide, the remainder being alumina.

(b) The following gas compositions were treated: (1) 5,000 ppm of CF₄ at

700°C, having a space velocity of 1000 hr⁻¹, for 2,000 hours; (2) 10,000 ppm of CF₄ at 750-760°C, having a space velocity of 1476 hr⁻¹, for 3,000 hours; and (3) 5,000 ppm of a gas containing CHF₃, CF₄, and C₄F₈ (10:10:1) at 700°C, having a space velocity of 990 hr⁻¹, for 4612 hours.

(c) The results of the experiments are shown on the attached sheet and show that the catalysts of the present invention unexpectedly exhibit excellent catalytic activity for a long time.

(d) The alumina-nickel oxide catalysts surprisingly maintained a catalytic activity of greater than 99% for over 2,000 hours when treating CF₄. Similarly, the alumina-nickel oxide catalysts surprisingly maintained a catalytic activity of greater than 98% for over 4,000 hours when treating a gas containing CHF₃, CF₄, and C₄F₈. This represents at least a 5-fold and 10-fold increase, respectively, in catalyst life over the longest run of 400 hours disclosed in Example XVII of Rossin.

II. CONDITIONS FOR TREATING FLUORINE-CONTAINING COMPOUNDS

6. Hitachi has provided plants containing catalysts for the decomposition of fluorine-containing compounds to many semiconductor manufacturers. In the semiconductor manufacturing processes, a fluorine compound concentration ranges from about 5,000 ppm to 10,000 ppm; the reaction temperature for decomposition is from 700 to 760°C; and the space velocity ranges from about 1,000 to 1,500 h⁻¹. These conditions are typically found in semiconductor and liquid crystal display device manufacturing plants.

7. One skilled in the art would have expected a rapid deterioration of catalytic activity during treatment of a gas having a concentration of 5000 ppm of a fluorine compound. This high concentration is typically encountered in commercial applications rather than a lower fluorine compound concentration of only 500 ppm as disclosed in Rossin. The low concentration used in Rossin is not meaningful for commercial applications, such as semiconductor and liquid crystal manufacturing plants and the like, with which our present invention is concerned.

8. In Example XIX of Rossin, wherein 5,000 ppm of CF_4 is treated, an initial conversion rate at 700°C is only 65.8%. An initial conversion rate at 750°C is 97.4%. In contrast, an initial conversion rate of the alumina-nickel oxide catalyst of the present invention is 99%. Further, the conversion rate after 8,000 hours is at least 99% for a gas containing 5,000 ppm CF_4 at 700°C . This is a surprising and unexpected result.

III. USE OF CLAIMED ALUMINA-NICKEL OXIDE CATALYST IN SEMICONDUCTOR AND LIQUID CRYSTAL MANUFACTURING PLANTS

9. Hitachi, Ltd. first placed a plant utilizing a catalytic decomposition process of fluorine-containing compounds with an alumina-nickel oxide (26.8 wt.%) catalyst in a semiconductor manufacturing plant in March 1999. This was a research and development decomposition plant.

10. In July 1999, Hitachi, Ltd. provided a commercial decomposition plant for a semiconductor manufacturing plant in New Jersey. Through the rest of 1999, an additional 6 semiconductor plants were equipped. In 2000, 42 semiconductor manufacturing plants were equipped with a catalytic decomposition process for fluorine-containing compounds. All the catalysts used were alumina-nickel oxide catalysts. None of the plants, which are typically operated on a continuous basis, have yet required replacement of the catalysts due to its unexpected and superior catalyst life.

11. As of January 2002, 118 gas-treatment plants for semiconductor and liquid crystal display device manufacturing plants worldwide use the alumina-nickel oxide catalysts according to the present invention to eliminate the hazardous environmental effect of fluorine-containing compounds. Moreover, because the catalysts according to the present invention have a superior catalytic life, the reactors for treating the fluorine-containing compounds have much less operating costs than plants using a combustion process or alkaline solution absorption process. Further, the process according to the present invention has excellent safety of operation compared to combustion processes.

IV. AWARDS

12. Hitachi, Ltd. has received many awards from both the government and private sectors recognizing the outstanding results obtained by using the claimed aluminum-nickel oxide catalyst.

For example, an abatement system using the claimed catalyst received the U.S. Environmental Protection Agency's Climate Protection Award in 2002, which will be awarded on March 25, 2002, as shown by the attached letter. In addition, Hitachi received the Semiconductor International Editor's Choice Best Products Award of 2001. A copy of this award is attached.

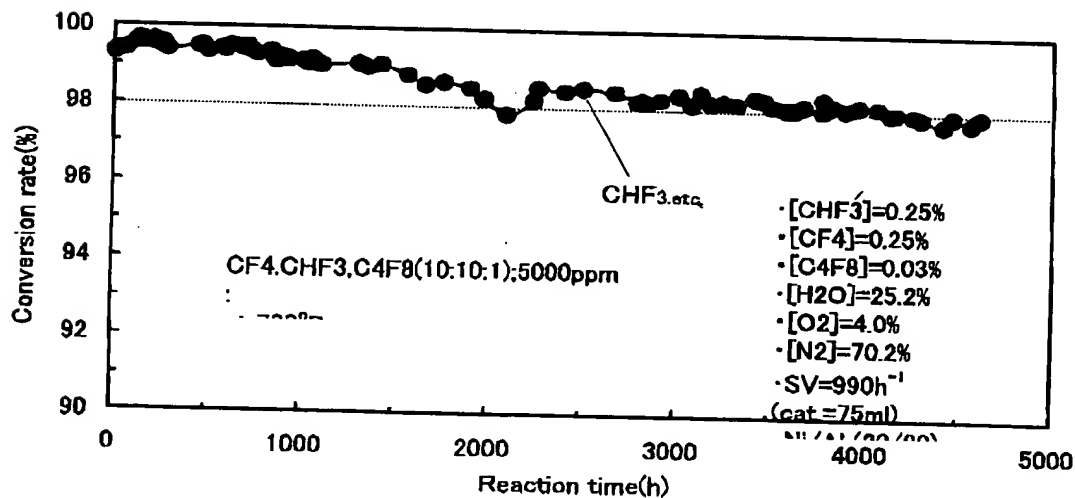
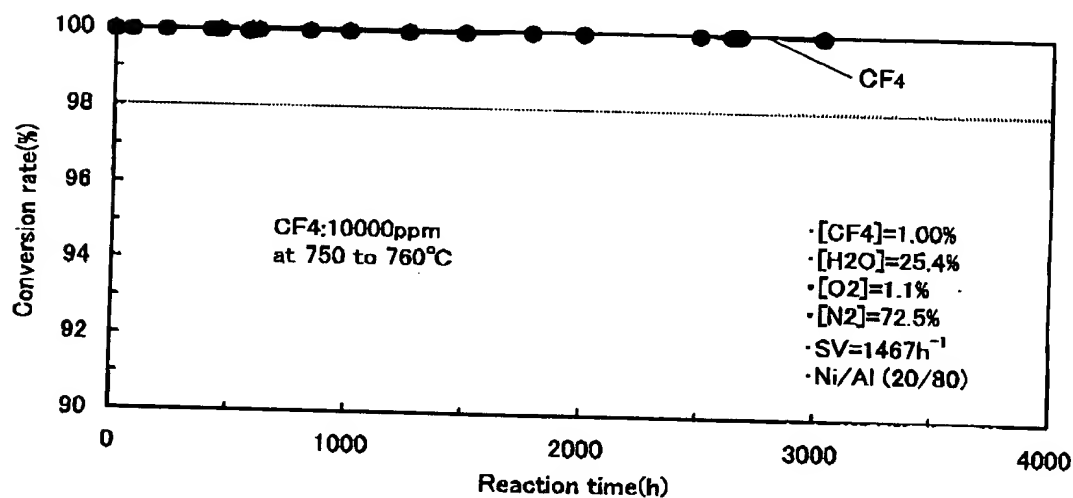
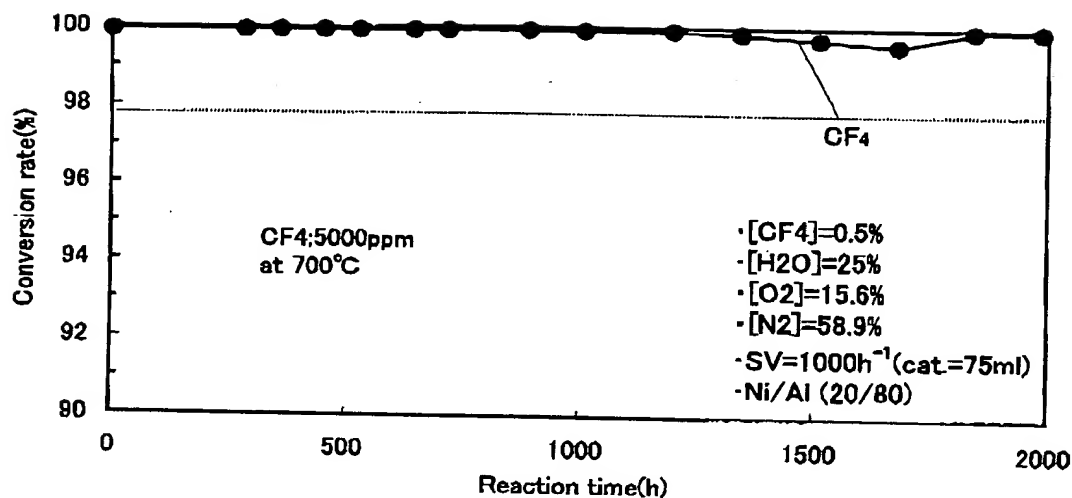
Further, Hitachi, Ltd. has received an award from the Department of Industrial Technology and Environment of Ministry of Economy and Industry of Japan (former MITI) in June 2001. The award was given because Hitachi's abatement plant was recognized as a technology that has greatly contributed to environment protection and development of environment plant industry because of its high quality and performance.

Hitachi, Ltd. has also received an award from Daily Industry News, Inc. and Environment Survey Center, Inst. in June 2000 for the contribution to environment protection.

13. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true, and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful statements may jeopardize the validity of the application or any patent issuing thereon.

Feb. 7, 2002
DATE

Shuichi Kanno
SHUICHI KANNO





UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

January 11, 2002

OFFICE OF
AIR AND RADIATION

Taku Nakajima
Hitachi, Ltd.
6, Kanda-Surugadai 4-chome, Chiyoda-ku
Tokyo 101-8010, Japan

Dear Taku Nakajima,

The Environmental Protection Agency is pleased to inform you that you have been selected to receive the 2002 U.S. Environmental Protection Agency's Climate Protection Award. You are one of 20 individuals, organizations and teams internationally to receive this honor in recognition of exemplary efforts and achievements in protecting the climate. Winners are from five countries: Canada, Chile, Italy, Japan, and the United States.

The Awards were evaluated by EPA staff and judged by an international panel representing industry, government, and international non-governmental organizations. EPA made the final selection of award winners.

The award will be presented at an awards dinner on the evening of Monday, March 25, 2002, during the Earth Technologies Forum in Washington, D.C. The dinner will take place at the Hyatt Regency on Capitol Hill, 400 New Jersey Avenue, N.W., from 7:00 PM until 10:00 PM. There will be a photographer at the dinner to take photographs of the award winners. You may also wish to consider the advantage of scheduling photographs in an unhurried atmosphere during the afternoon. EPA will do its best to accommodate your requests.

Attached are several documents that provide further details regarding the awards.

Sincerely,

Caley Johnson

Director of Climate Protection Awards
Climate Protection Division

Internet Address (URL) - <http://www.epa.gov>

Recycled/Recyclable - Printed with Vegetable Oil Based Inks on Recycled Paper (Minimum 25% Postconsumer)

Attachment 6

2002 CLIMATE PROTECTION AWARDS SUMMARY OF AWARD WINNER'S ACCOMPLISHMENTS

The following summary was developed by the EPA. It will appear in an awards program book to be distributed at the awards dinner on March 25, 2002. Please edit the summary to be no longer than 100 words and fax the edited summary to Meagan Johnston at the number below.

PFCs are powerful greenhouse gases with long lifetimes due to their molecular stability. In 1998 Hitachi successfully developed a way to decompose these molecules through catalysis, and that process is now being used widely by semiconductor and liquid crystal display manufacturing industries. Before this invention, there were no economical means of destroying PFCs. The Hitachi Super Catalytic Decomposition System is proven to be >99% efficient at decomposing all PFC gases while maintaining a low cost of ownership to the operational facility.

**Please fax this form by *January 25, 2002* to Meagan Johnston at 202 862-1144.
If you have any questions, call Meagan Johnston at 202-862-1110 or send an e-mail
to mjohnston@icfconsulting.com.**

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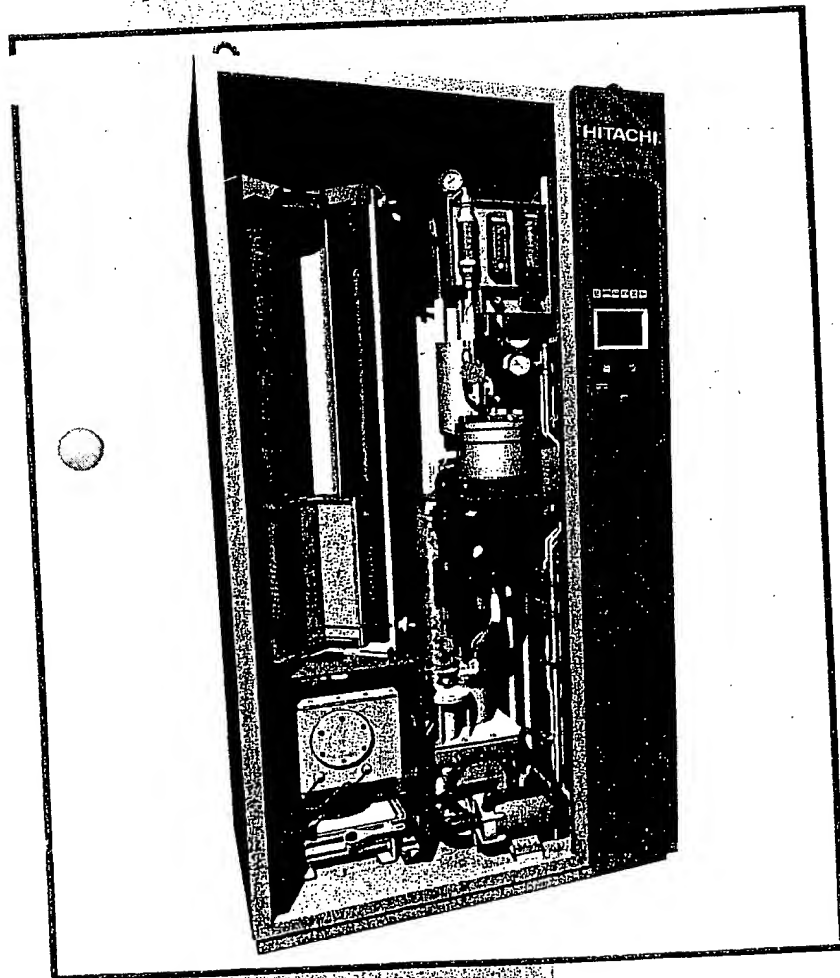
EDITORS'
CHOICE

2001

Editors'
Choice

Best Products Award

Hitachi SCDS
Catalytic PFC
Abatement System



Hitachi America, Ltd.



The editors of
Semiconductor International
magazine honor products that
have the following qualifications:

- ▶ Advanced wafer processing, chip assembly, packaging or testing capabilities;
- ▶ Enhanced semiconductor or related manufacturing results.
- ▶ Improved employee productivity or working conditions; or
- ▶ Aided manufacturer's efforts to provide a safer workplace or environment.

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2001 Editors' Choice Best Product Awards

Maria A. Lester, Associate Editor; Aaron Hand, Managing Editor — *Semiconductor International*, 12/1/2001

Since 1989 *Semiconductor International* has been honoring proven semiconductor or related manufacturing products in our Editors' Choice Best Product Awards program. This program recognizes superior performance of equipment, materials, software and other products that advance wafer processing, chip assembly or packaging, or process testing capabilities; enhance semiconductor or related manufacturing; improve employee productivity or working conditions; or help a manufacturer to provide a safer workplace or to be more environmentally responsible. *Semiconductor International* chose 20 products used in the semiconductor and related manufacturing industries to honor for excellence.

At a Glance

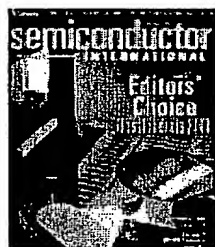
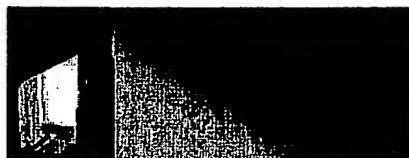
The Editors' Choice Best Product Awards program, established in 1989, recognizes 20 products used in semiconductor and related manufacturing every year. All of this year's winners were nominated by users, and comments from users were used in the evaluations. This year's Grand Award winner is the eS20XP e-beam wafer inspection system from KLA-Tencor.

The program differs from other product awards in that users must nominate products. One or more knowledgeable users nominated all 20 products presented on the following pages, and *Semiconductor International's* editors used their extensive comments to help choose the winners.

The editorial staff of *Semiconductor International* congratulates all the winners, presented here in alphabetical order by company. We urge users to nominate products for next year's program. Eligible products include equipment, materials, software or related products used to manufacture semiconductors, MEMS devices, flat-panel displays or related goods. Further information can be found on our [Web site](#).

Semiconductor International recognizes that competitive advantages are associated with the use of these products, and we keep all information provided strictly confidential. Though it is necessary to confirm that valid users nominate products, information obtained will not be used as an endorsement. Confidentiality is scrupulously maintained to allow users to nominate deserving products and give honest opinions.

Grand Award: KLA-Tencor



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Tools and Services

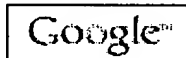
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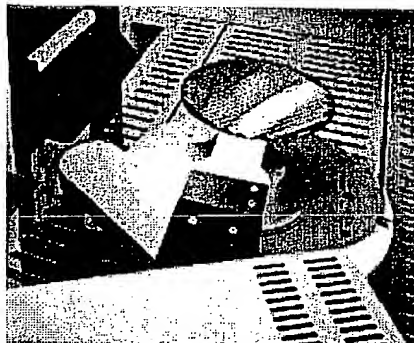
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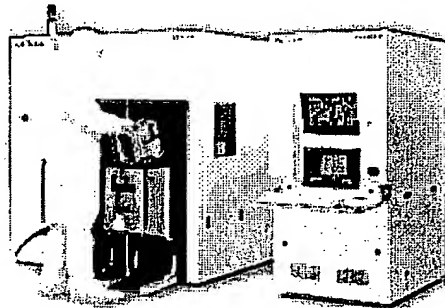
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Grand Award: KLA-Tencor

The eS20XP scanning e-beam wafer inspection system from KLA-Tencor (San Jose) was this year's Grand Award winner. Using state-of-the-art voltage contrast capability, it detects electrical defects during front-end processing, inspecting an entire wafer in little more than an hour compared with days required by previous-generation and competitive e-beam systems. Because it enables fab engineers to find electrical defects at the source layer instead of at back-end electrical test, the tool dramatically reduces the risk of weeks or months of work in progress (WIP) to exposure to these yield-killing defects. The eS20XP detects physical defects as small as 50 nm, as well as defects in high-aspect-ratio structures

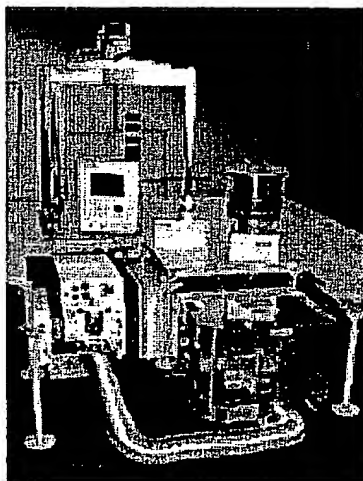


Grand Award winner – KLA-Tencor Corp., eS20XP



Alcatel Vacuum Technology

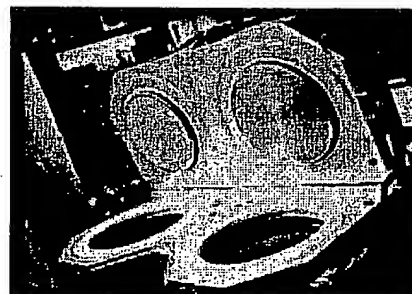
The CPM Etch 2610 APC tool from Alcatel Vacuum Technology (Annecy, France) is one of a family of chamber pressure management systems for dry etch tools, designed to reduce device defectivity by lowering particulate levels in the process chamber. It is a complete vacuum and abatement system (from the process chamber isolation valve to atmospheric exhaust of treated effluent) with variable speed control that allows process pressure control during etch processing without the use of the isolation valve's throttling function.



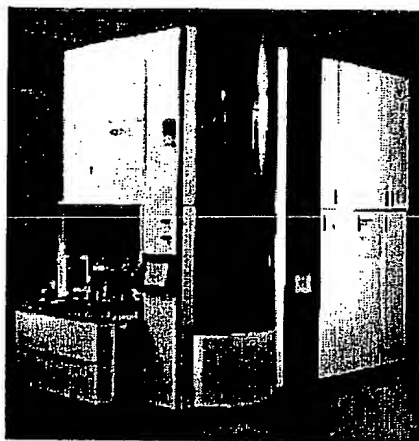
Alcatel Vacuum Technology, CPM Etch 2610

Applied Materials

SACVD (sub-atmospheric chemical vapor deposition) processing from Applied Materials (Santa Clara, Calif.) uses Ozone-TEOS technology to deposit silicon glass (SiO_2) for various front-end gap fill applications. SACVD films are used primarily in pre-metal, inter-metal and STI gap fill applications in advanced memory, flash, and logic devices. SiO_2 films deposited by SACVD have exceptionally low impurities and stress, along with excellent high-aspect-ratio gap fill capability.



Applied Materials Inc., SACVD process



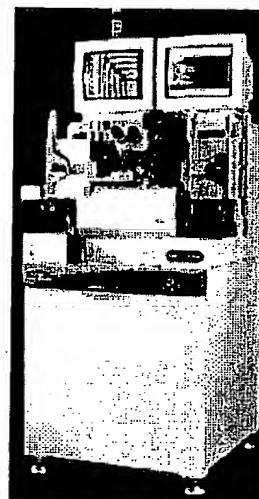
ASM International, Advance A400 Series

ASM International

The Advance A400 Series from ASM International (Bilthoven, Netherlands) is a family of vertical furnaces grouped around two main products: the A400 and A412 furnaces. The A400 supports 200 mm wafers, and the A412 handles both 200 and 300 mm wafers. The furnaces are used in wafer processing for diffusion, oxidation and LPCVD applications. Primary atmospheric applications are dry and wet oxidation, anneal, POCl_3 and BBr_3 . The main LPCVD applications are TEOS and poly (doped and undoped), nitride, SHG, DCS- and SiH_4 -based HTO, and oxynitride.

ASM Technology

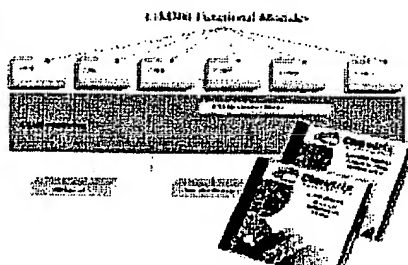
The AB339Eagle automatic gold wire ball bonder from ASM Technology (Singapore) is used to provide the electrical interconnection between die pads to the connecting leads. With an accuracy of $\pm 0.37 \mu\text{m}$, it is key in wire bonding processes with ultrafine pad pitch requirements. It has also been improved over its AB339 predecessor with the use of linear motors to minimize maintenance and lightweight bond heads to achieve higher bonding speeds.



ASM Technology, AB339Eagle

Cimetrix

CIMConnect and CIM300 from Cimetrix (Salt Lake City) provide the ability for semiconductor equipment to communicate with a factory host. CIMConnect is an object-oriented service toolkit with SECS/GEM

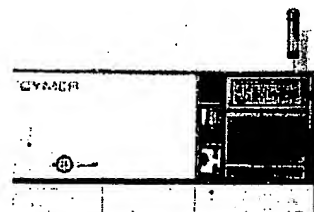


Cimetrix Inc., CIMConnect & CIM300

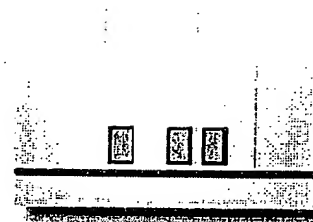
capability, providing a generic mechanism by which data can be uploaded from factory equipment to a factory host, and processing instructions can be downloaded from host to equipment. CIM300 provides support for the SEMI 300 mm communications standard. The architecture consists of a foundation module that provides compatibility to selected SECS/GEM products and provides a consistent interface for the functional modules.

Cymer

The ELS-6010 248 nm 2.5 kHz excimer laser from Cymer (San Diego) is for photolithography applications. Aimed at 130 nm process development and device manufacturing, it has a line-narrowed bandwidth of 0.5 pm FWHM and 1.4 nm at 95% energy, and enables the use of



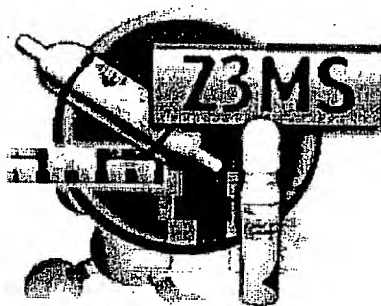
...at low energy, and enables the use of high-NA lenses (>0.70). The laser provides 25% more pulses than 2 kHz systems, dose stability, CD control and high yield.



Cymer Inc., ELS-6010

Dow Corning

The Z3MS CVD precursor from Dow Corning (Midland, Mich.) is a versatile, high-performance precursor that is compatible with copper damascene and aluminum applications. This PECVD technology is

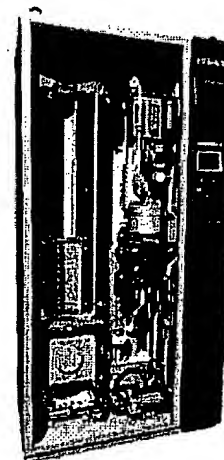


designed for use with existing equipment and processes. It has a $k=2.7$ and the same one-chamber processing technology developed for silane-based dielectric film deposition. The material offers performance-enhancing benefits for film applications including copper diffusion barrier, gap fill (3:1 AR, 0.2 μm gaps), damascene etch-stop (selectivity $>2 \times \text{SiN}$), and improved passivation (SiC). It is a non-corrosive, non-pyrophoric, organosilicon gas.

Dow Corning Corp.,
Z3MS

Hitachi America

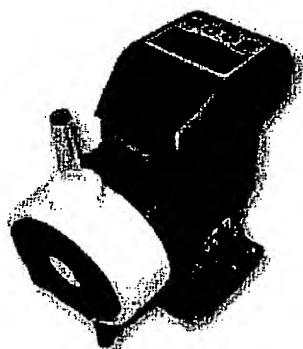
The SCDS catalytic system from Hitachi America (Dallas) is designed for semiconductor PFC abatement. The system features catalytic decomposition technology that produces less waste and has a lower cost of ownership than reclaim combustion or chemical conversion methods. The majority of semiconductor process gases can be abated with better than 99% efficiency. Spent catalyst cartridges are then recycled in steel manufacturing.



Hitachi America
Ltd., Hitachi SCDS

Iwaki Walchem

The EH-FF electronic metering pumps from Iwaki Walchem (Holliston, Mass.) allow users to accurately mix, blend or replenish ultrahigh-purity fluids. The pump



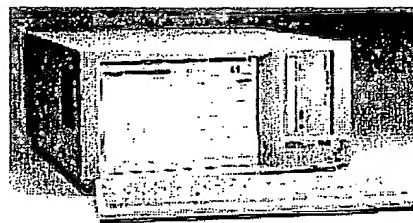
dispenses the fluid more times, in smaller amounts, allowing better mixing and more control of the process. It was designed for the semiconductor manufacturing environment. Applications include on-tool chemical generation such as SC1, SC2, dilute RCA cleans, buffered oxide etches and new semi-aqueous cleaning solutions. It is powered by 115 or 220 V and can accept analog or digital inputs. Fluid connections are PFA tubes that accept all popular flared fittings.

Iwaki Walchem Corp., EH-
FF

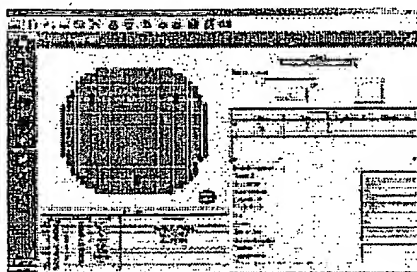
Instruments

Keithley

The Model 4200-SCS semiconductor characterization system from Keithley Instruments (Cleveland) provides lab-grade dc device characterization with real-time plotting and analysis. The instrument structure allows simultaneous measurement of up to eight measurement channels and software that requires only one mouse click to move between tests. The built-in software supports setup, data collection, analysis and data storage. It supports CV meters, switching matrixes and related test equipment. It is available in several configurations for local or remote sense.



Keithley Instruments Inc., Model 4200-SCS



Kinesys Software, ALPS

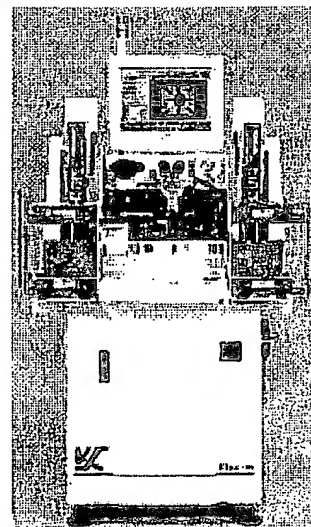
Kinesys Software

ALPS wafer map software from Kinesys Software (Petaluma, Calif.) is targeted at inkless assembly applications, providing wafer map data management and equipment integration from wafer sort to die attach. It communicates with production equipment, human users, and proprietary or commercial manufacturing execution systems. Information is collected from the sources, combined

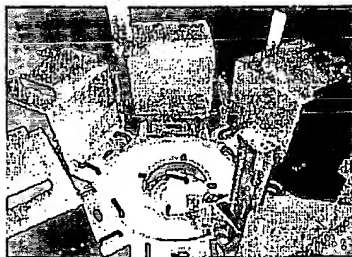
and stored in the ALPS relational database and made available on request to the same parties, to support efficient, error-free and traceable production. Information processed includes wafer maps, sort lots, assembly lots, wafer-to-frame relationships, die-level material tracking data, etc.

Kulicke & Soffa

The Max μ m automatic ball bonder from Kulicke & Soffa (Willow Grove, Pa.) offers 65 msec standard wire cycle speed, which equates to >15 wires/sec. It supports 45 μ m production-level process capability. Features include a high-performance X-Y table with 56 x 66 mm bonding, a Precision-Touch bond head with a new Z-axis link, a μ T-Sonics ultrasonic transducer and Pro-Pulse wire clamp technology. Its enhanced dual mag ultrafine pitch optics include a standard third programmable LED source for extended illumination, providing die-tilt-tolerant imaging.



Kulicke & Soffa, Max μ m



Lam Research

The 2300 Versys Silicon etch system from Lam Research (Fremont, Calif.) is for 200 and 300 mm wafers. Its small-footprint, open-architecture platform handles four process modules and enables advanced factory and process automation. Part of a series that

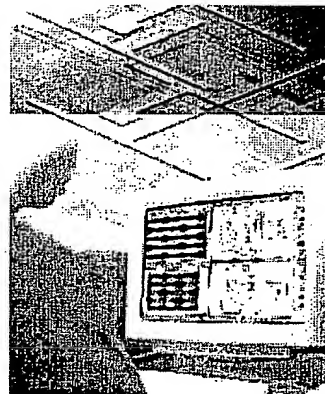


Lam Research Corp., 2300
Versys Silicon

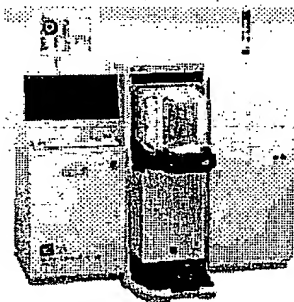
supports all etch applications for sub-130 nm nodes, the Versys Silicon is for in situ waferless auto cleans for high mean time between wet cleans with interferometric endpoint detection optional.

Numerical Technologies

The Virtual Stepper System from Numerical Technologies (San Jose) is a photomask qualification tool. It is an integrated software solution that determines the impact of mask defects by separating true defects from nuisance defects. It provides advanced defect printability analysis and mask quality control capabilities, and can be used for through-repair and post-repair verification. Virtual Stepper helps to reduce mask cost and manufacturing cycle time by automating what has been a manual, labor-intensive step in the manufacturing process.



Numerical Technologies
Inc., Virtual
Stepper System



QC Solutions Inc., QCS-
7000 Series

QC Solutions

The QCS-7000 Series Surface Charge Profiler from QC Solutions (Billerica, Mass.) is used to monitor the doping concentration (or resistivity) in silicon epitaxial processes. It is an in-line metrology tool that is both non-contact and non-destructive, with high throughput capability. It replaces traditional analytical measurement tools such as CV and 4-point probes, which require that test wafers be scrapped.

Thermo Nicolet Industrial Solutions

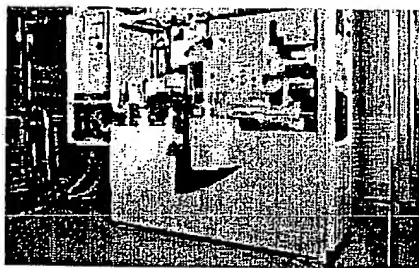
The ECO 1000 FTIR metrology tool from Thermo Nicolet Industrial Solutions (Madison, Wis.) is a fourth-generation wafer analysis system. It uses a Fourier transform infrared (FTIR) spectrometer designed specifically to enhance the spectroscopic analysis of semiconductor wafers. A dynamically aligned, frictionless bearing interferometer allows users to switch between reflectance and transmission measurements by software command. The system produces multiple point measurements, referenced to either flats or notches, in transmission and reflectance modes using the preprogrammed SEMI standard patterns or a user-defined special pattern.



Thermo Nicolet
Industrial
Solutions, ECO 1000



Trikon
Technologies



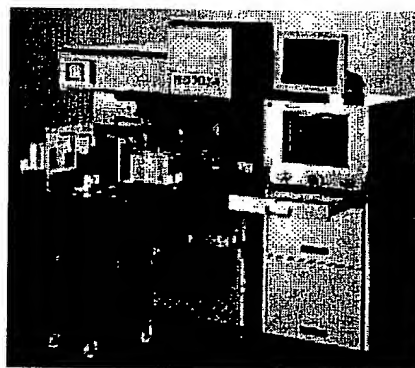
Trikon Technologies, Omega 201

The Omega 201 plasma etcher from Trikon Technologies (Newport, UK) is used for a range of critical etch processes in fabricating silicon, III-V and optical waveguide devices. It offers three plasma source technologies on a common hardware set for diverse applications: MORI, a high-density helicon; plasma-enhanced reactive ion etch (PERIE); and inductively coupled

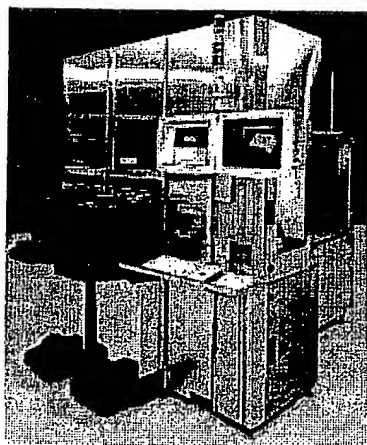
plasma (ICP). The Omega 201 incorporates Trikon's unique electrostatic chuck (ESC), which avoids the use of mechanical clamps that can introduce particles and defects into materials.

Ultratech Stepper

The Model 1600DSA stepper from Ultratech Stepper (San Jose) is designed for microelectromechanical systems (MEMS), micro-optoelectromechanical systems (MOEMS) or micromachining applications. The tool is equipped with dual-side alignment capability for processing both sides of the wafer. It has 1.0 and 2.0 μm resolution lens options. Features include a high wafer plane irradiance for improved process throughput; process flexibility such as a large depth of focus; non-standard substrate handling, and custom hardware and software for thick resist processing; and the company's machine vision system for flexible alignment capability.



Ultratech Stepper Inc., Model 1600DSA



Veeco Metrology Group, Dimension Vx330

Veeco Metrology Group

The Dimension Vx330 atomic force profiler (AFP) from Veeco Metrology Group (Santa Barbara, Calif.) is suited to CMP process characterization and production monitoring as well as non-destructive depth measurement of high-aspect-ratio features. The Vx330 AFP mode enables non-destructive automated measurement of dishing, erosion and step height with high resolution, repeatability and accuracy. It complies with relevant standards for fully automated operation in a 300 mm production environment.

For more information...

When you contact any of the following manufacturers directly, please let them know you read about them in Semiconductor International.

Alcatel Vacuum Technology

Applied Materials

ASM International

ASM Technology

Cimetrix

Cymer

Dow Corning

Hitachi America

Iwaki Walchem

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